

# **Exhibit A**

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# **Metals Handbook<sup>®</sup> Ninth Edition**

## **Volume 9 Metallography and Microstructures**

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# Solidification Structures of Aluminum Alloy Ingots

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ALUMINUM ALLOY INGOTS intended for subsequent rolling, extruding, or forging are considered in this article. Ingots intended for remelting and shaped castings produced in foundries are not discussed, although their solidification structures are similar to those of ingots for working.

## Dendrites

Dendritic solidification macrostructure is characteristic of all aluminum alloy castings. A variety of such structures in sand, permanent mold, investment, and die castings are shown in Fig. 103 to 179 in the article "Aluminum Alloys" in this Volume. Dendrites in aluminum alloy welds and brazed joints are shown in Fig. 180 to 229 in the same article.

The first systematic attempt to relate dendritic solidification to casting conditions for a number of aluminum alloys was reported in 1950 (Ref 1). It was established that the spacing between adjacent arms in dendrites decreases as solidification time decreases. Subsequent investigations have confirmed this result (Ref 2); data from a selection of published papers are shown in Fig. 1. The rela-

tionship between dendrite arm spacing and solidification time is given by the equation:

$$d = 7.5\theta^{0.37} \quad (\text{Eq. 1})$$

where dendrite arm spacing ( $d$ ) is in microns and solidification time ( $\theta$ ) is in seconds. Constants depend on the alloy in question, but equations of this form have been shown to fit extensive data from the aluminum-copper system.

The influence of solute content is less well defined. In general, up to eutectic compositions, the effect of increasing solute content at a constant freezing rate is to decrease dendrite arm spacing (Fig. 2). The relationship between solute content and dendrite arm spacing has been well documented also for steel and for copper alloys, as described in the articles "Solidification Structures of Steel" and "Solidification Structures of Copper Alloy Ingots" in this Volume.

Fine and coarse dendritic structures typical of aluminum alloy ingots are illustrated in Fig. 3 and 4, respectively. Fine dendrite arm spacing is usually associated with a uniform distribution of small constituent particles and generally is preferred. However, fine spacing is not always compatible with the desired

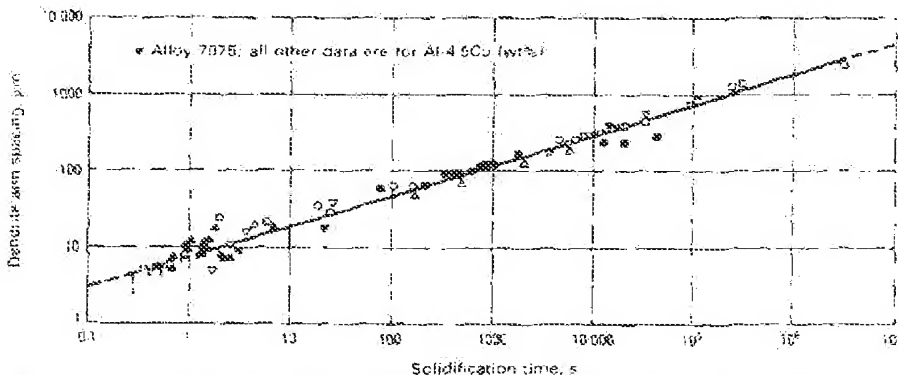
grain structure. In general, dendrite arm spacing is most important in ingots of heat-treatable alloys and in ingots that are cast close to final part size and shape and thus subjected to a minimum of deformation during subsequent fabrication.

## Grain Structure

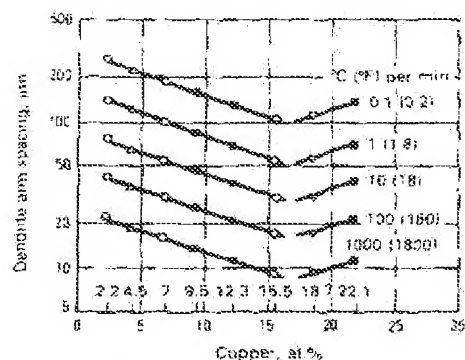
Grain size is an important, readily observed feature of aluminum alloy ingots. A uniform, fine grain size is sought in most instances to obtain optimum properties in the wrought product. Grain refinement also increases resistance to hot cracking during casting.

The columnar grain structure shown in Fig. 5 is characteristic of a low-solute alloy that has solidified in a steep temperature gradient with little turbulence in the melt to effect grain refinement by detachment of dendrite arms. In the presence of turbulent directed metal flow, the structure of such an alloy would consist of columnar and equiaxed grains, as illustrated in Fig. 6.

**Grain Refining.** The addition of a grain refiner resulted in the nearly equiaxed struc-



**Fig. 1** Effect of solidification rate, as measured by solidification time, on secondary dendrite arm spacing of castings of aluminum alloys 7075 and Al-4.5Cu (wt%). The log-log plot includes data from nine investigations indicated by nine symbols.



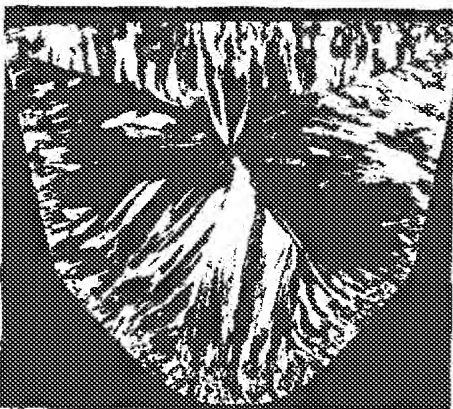
**Fig. 2** Effect of copper solute content (internal scale) on secondary dendrite arm spacing in eight aluminum alloys, as plotted for five cooling rates. (Ref 3)



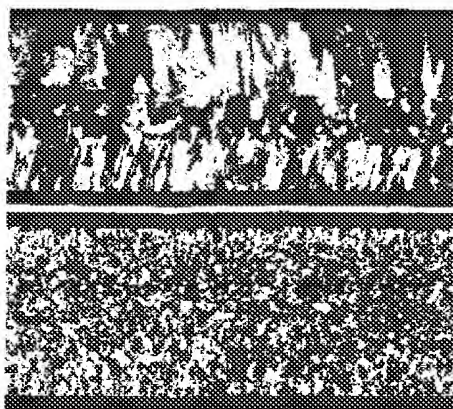
**Fig. 3** Direct-chill semicontinuous cast alloy 3003 ingot. Solidification time of approximately 1 s produced fine dendrite arm spacing, as shown by the interdendritic network of manganese-bearing constituents (dark). See also Fig. 4. Keller's reagent, 500 $\times$



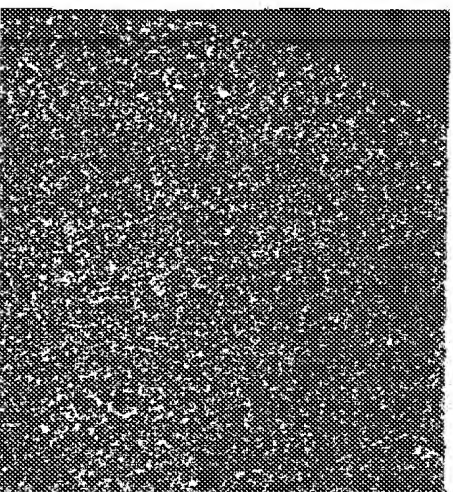
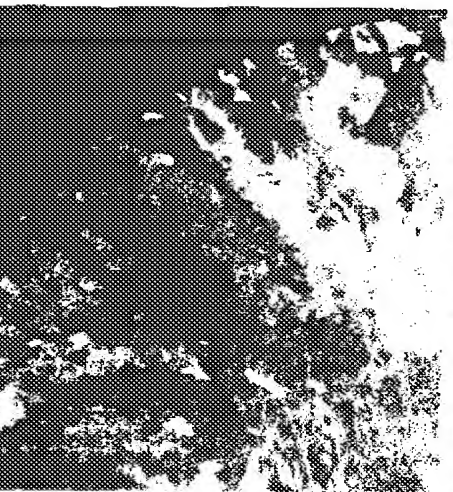
**Fig. 4** Same as Fig. 3, except that solidification was approximately 10 s, which produced coarser dendrite arm spacing than in Fig. 3. Note that the manganese-bearing constituents are also coarser. Keller's reagent, 500 $\times$



**Fig. 5** Transverse section through an ingot of alloy 1100 that was cast by the Properzi (wheel-and-belt) method. Note the consistency with which columnar grains have grown perpendicularly to each face of the mold. Tucker's reagent, 11/2 $\times$



**Fig. 6, 7** Longitudinal sections through 25-mm (1-in.) thick slabs of alloy 1100 cast by the Hazlett (two-belt) method. Upper slab (Fig. 6) was cast without a grain refiner; lower slab (Fig. 7), with a grain refiner. Tucker's reagent. Actual size



**Fig. 8, 9** Portions of transverse sections through two 150-mm (6-in.) diam ingots of alloy 6063 that were direct-chill semicontinuous cast. Fig. 8: Ingot was cast without a grain refiner, note columnar grains and colonies of featherlike crystals near the center of the section. Fig. 9: Ingot, which shows a fine, equiaxed grain structure, was cast with a grain refiner. Tucker's reagent. Actual size

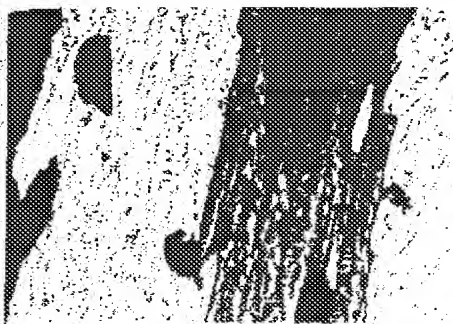
ture shown in Fig. 7. The grain-refining inoculants commonly used in the aluminum industry are master alloys containing titanium or titanium plus boron (Ref. 4-7). It is common practice to add grain-refining master alloy in the form of a 9.55-mm (0.38-in.) diam rod continuously to the molten metal as it flows from the holding furnace to the casting unit. Grain-refining additions are used to obtain a fine, uniform grain structure and to reduce the formation of center cracks. The coarse, nonuniform structure obtained in alloy 6063, which was cast without a grain refiner added to the melt, is shown in Fig. 8. The dramatic reduction in grain size and improvement in structure uniformity as a result of adding a grain refiner is shown in Fig. 9.

The conflict that may exist between obtaining a fine dendritic structure and a uniform, small grain size is illustrated in Fig. 10 and 11. Cast without a grain refiner, an ingot exhibits fine dendrite spacing but wide, columnar grains (Fig. 10). By contrast, a somewhat coarser dendritic structure with much smaller, equiaxed grains is illustrated in Fig. 11, which shows a section from an ingot cast with a grain refiner.

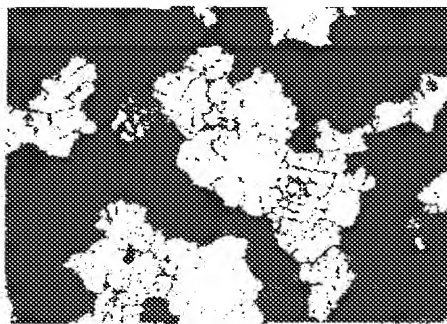
Grain size may be controlled by such methods as vibration, stirring, and control of metal flow, which provide nuclei by detachment of dendrite arms. A successful application of the latter method has been reported in Ref. 8. The fully columnar structure produced when the metal feed is located at the center of the mold cavity is illustrated in Fig. 12. When the stream is directed across the solidifying shell of the casting, the largely equiaxed structure shown in Fig. 13 is obtained.

**Twinned Columnar Growth (Feather Crystals).** Aluminum alloy ingots cast without a grain refiner often exhibit a fan-shaped columnar structure, referred to as "feather crystals." This structure, illustrated in Fig. 14 (see also Fig. 8), may be found in low- and high-solute alloys. It is most likely to develop when there is a steep thermal gradient ahead of the solidifying interface (Ref. 8) or an inadequate addition of grain refiner (Ref. 9). At higher magnification, the feather crystals consist of twinned columnar grains (Fig. 15).





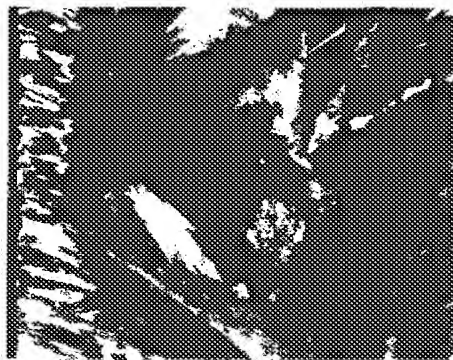
**Fig. 10** Wide, columnar grains and fine dendrite arm spacing in alloy 6063 ingot cast without a grain refiner. Polarized light. Compare with Fig. 11. Barker's reagent. 40×



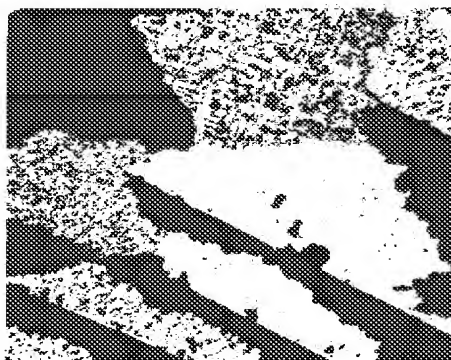
**Fig. 11** Same as Fig. 10, except cast with a grain refiner. Note small, equiaxed grains and increased dendrite arm spacing compared with Fig. 10. Polarized light. Barker's reagent. 40×



**Fig. 12, 13** Transverse slices through portions of two continuously cast 75 × 100-mm (3 × 4-in.) 1 section ingots of alloy 1100 illustrating the effect of metal-feed location on structure. Fig. 12: the liquid metal entered at the center of the section. Fig. 13: the metal-feed location caused a flow of hot metal across the solidifying shell. Modified aqua regia (50 ml. HNO<sub>3</sub>, 50 ml. HCl). Actual size. (Ref. 8)



**Fig. 14** Portion of a longitudinal section through a 75-mm (3-in.) diam alloy 1100 ingot, direct-chill cast without a grain refiner. Center of section contains fan-shaped zones of feather crystals. Tucker's reagent. Actual size.



**Fig. 15** Feather crystals in an alloy 3003 ingot that was cast by the direct-chill semicontinuous process. Growth twins in the crystals have been revealed by photographing the specimen with polarized light. Barker's reagent. 50×

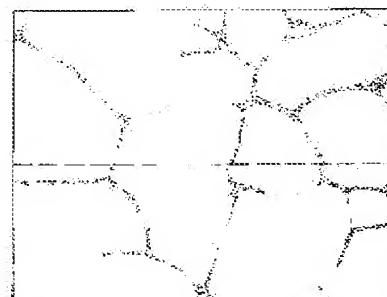
## Microsegregation

Most of the major alloying additions made to aluminum are less soluble in the solid phase than in the liquid phase; that is, the equilibrium distribution coefficient ( $k_e$ ) is less than 1 (see the article "Solidification Structures of Solid Solutions" in this Volume). Moreover, for most solutes, aluminum exhibits a relatively low terminal solid solubility; therefore, second-phase constituents are invariably present in ingot structures. For these reasons, the dendrites, which are the first portions of a cast structure to solidify, are low in solute content and are surrounded by interdendritic networks of one or more second-phase constituents. The size and distribution of the constituents depend on such factors as solute concentration, dendrite arm spacing, and grain size. The solute distribution characteristic of cast alloys, referred to as "coring," may be described (Ref. 10) with reasonable accuracy by the Scheil equation:

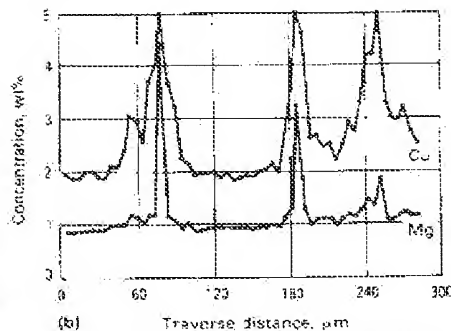
$$C_s = C_o k_e (1 - f_s)^{k_e - 1} \quad (\text{Eq. 2})$$

where  $C_o$  is the concentration of a solute in the alloy,  $k_e$  is the equilibrium distribution coefficient, and  $C_s$  is the composition at weight fraction solid  $f_s$ .

Copper and magnesium microsegregation in a 2124 direct-chill cast ingot, observed using electron probe microanalysis, is shown in Fig. 16. The path traversed by the electron



(a)



(b)

**Fig. 16** Copper and magnesium microsegregation in a direct-chill semicontinuous cast (810 × 1372 mm, or 24 × 54 in.) 2124 alloy ingot. (a) Dendrite cells at midthickness location in ingot and enrichment of copper and magnesium at the cell boundaries. When observed in conjunction with the electron probe microanalysis, the gradual increase in solute concentration across the dendrite cell is readily apparent. (b) Microprobe traverse across dendrites.